UDC 544.31:546.56’289’811/23

DETERMINATION OF THERMODYNAMIC FUNCTIONS OF PHASE TRANSITION OF Cu_8SiSe_6 COMPOUND BY THE DSC METHOD

U.R. Bayramova

Institute of Catalysis and Inorganic Chemistry of Azerbaijan National Academy of Sciences,
AZ 1143, H. Javid ave., 113 Baku, Azerbaijan
e-mail: ubayramova088@gmail.com

Received 11.02.2022
Accepted 12.04.2022

***Abstract**: The ternary compound Cu8SiSe6 was studied by differential scanning calorimetry (DSC). Based on the data of DSC curves for two samples with different masses, the temperature and enthalpy of the phase transition from the low-temperature orthorhombic modification to the high-temperature cubic modification were determined. Using the Gibbs-Helmholtz equation, the entropy of the phase transition of the studied compound was also calculated.*

***Keywords:** Cu_8SiSe_6, phase transition, enthalpy, entropy, differential scanning calorimetry.*
DOI: 10.32737/2221-8688-2022-2-116-121

Introduction

Compounds of the argyrodite family with the general formula $A_8B^{IV}X_6$ (where A-Cu, Ag; B^{IV}-Si, Ge, Sn; X-S, Se, Te) have a number of valuable functional properties and are the object of study by many research groups. These compounds are attractive in several respects. First, there are rich materials physics and materials chemistry phenomena in these phases derived from their hybrid crystal structure in which the partially occupied mobile A-sublattice interpenetrates a rigid network of BX_4 tetrahedra and isolated X ions [1-3]. Secondly, Ag/Cu based argyrodites show themselves as promising thermoelectric materials [4–9], which is largely explained by the hierarchical structure of chemical bonds, which allows the existence of highly concentrated and highly mobile Ag^+/Cu^+ ions distributed in a rigid polyanionic framework. On the other hand, due to the same structural feature, representatives of this class have mixed ion-electronic conductivity [10–12], which makes them very promising for use in the development of photoelectrode materials, electrochemical solar energy converters, ion-selective sensors, etc. Another attraction of argyrodites is that they tend to undergo multiple phase transitions, indicative of closely competing thermodynamic states, as the temperature rises. As a rule, high-temperature modifications crystallize in a cubic structure [1, 13], while low-temperature phases have a lower symmetry. The thermodynamic properties of these compounds, as well as more complex phases based on them, have been studied in a number of works [14–21]. However, there is almost no information on the thermodynamic properties of phase transitions in argyrodite phases.

The purpose of this work was to determine the thermodynamic functions of the phase transitions of the Cu_8SiSe_6 compound by differential scanning calorimetry (DSC). This method is considered to be one of the most accurate methods in thermal analysis, and modern DSC instruments have a wide range of possibilities with which one can obtain various results of the study.

The Cu_8SiSe_6 compound melts congruently at 1380 K and has a polymorphic transformation at a temperature of 355 K [22] (330 K according to [23]). In the high-temperature phase of this compound, which crystallizes in a cubic structure (Sp. gr. $F\bar{4}3m$), copper atoms are disordered, which contributes

to high ionic conductivity caused by the migration of copper ions [13]. At low temperature, the compound crystallizes in an orthorhombic system (Sp. gr. $Pmn2_1$) with the following parameters: a = 7,2835 (2) Å, b = 7,2185 (2) Å, c = 10,2281 (3) Å; Z = 2 [23].

We have not found any information on the thermodynamic properties of this compound.

Experimental part

We synthesized the Cu_8SiSe_6 compound by direct fusion of elementary components of high purity in evacuated (~10^{-2} Pa) and sealed quartz ampoules at a temperature of ~1400 K., High-purity elemental components manufactured by EVOCHEM ADVANCED MATERIALS GMBH (Germany) were used: copper wire (Cu-00022; 99.999%), silicon granules (Si-00004; 99.999%), selenium granules (Se-00002; 99.999%). Considering the high vapor pressure of selenium at the melting point of the synthesized compound, its synthesis was carried out in a two-zone regime. After synthesis, the sample was annealed at 770 K (100 h). Next, the ampoule was cooled very slowly in the temperature range of the polymorphic transformation of the compound (320–370 K), and then subjected to thermal annealing at 320 K (10 h). This was done in order to ensure the complete transition of the high-temperature phase to the low-temperature phase in order to minimize the error in enthalpy calculations. The synthesized compound was identified by DSC and X-ray diffraction technique (XRD).

XRD was performed at room temperature on a *Bruker* D8 ADVANCE powder diffractometer ($CuK\alpha_1$ radiation). The powder diffraction pattern of the compound (**Fig. 1**) confirmed the complete transition of the compound to the low temperature structure. As can be seen from **Fig. 1**, the reflection peaks obtained by us for the synthesized Cu_8SiSe_6 completely coincide with the X-ray data (*red lines*) of the orthorhombic structure of this compound from the crystallographic database.

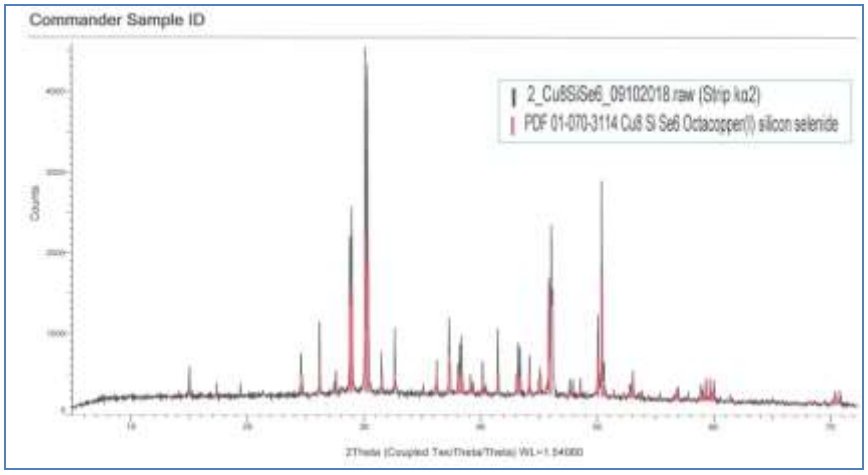

Fig.1. Powder diffraction pattern of the Cu_8SiSe_6 compound.

The temperature and heat of the phase transition of the Cu_8SiSe_6 compound were determined by DSC on a *Linseis* DSC400 differential scanning calorimeter. The measurements were carried out using the *Linseis TA V 2.3.1* software. The calorimeter was preliminarily calibrated. Considering that our studies will be carried out at low temperatures, relatively low-melting metals were used as standards for calibrating our device: indium, tin and zinc, provided by *Linseis* for this purpose. The temperature regime for the calibration of each of the substances was chosen by us in accordance with the recommendations given in the manual for the use of the device.

The DSC study of the Cu_8SiSe_6 compound was carried out using an aluminum crucible with a lid. Taking into account that the object of study is a solid polycrystalline sample, it was preliminarily ground into powder before measurement to ensure the maximum possible contact area between the sample under study and the bottom of the crucible. The heating rate was 3°/min. The DSC study mode was chosen taking into account the phase transition temperature of the studied compound.

Results and discussion

In order to improve the accuracy of the study, two samples of the Cu_8SiSe_6 compound with masses of 28.75 and 39.52 mg were selected, for which three DSC curves were taken in the dynamic heating mode from room temperature to 360 K. Further, the obtained DSC curves were processed using the *Linseis TA Evaluation V2.3.1* software and the temperatures of the beginning (T_{onset}) and end (T_{end}) of the peak, as well as the enthalpy of phase transition for 1 mole of the substance ($\Delta H_{p.t.}$) were obtained. As an example in **Fig. 2** shows one of the heating curves for a sample with a mass of 28.75 mg. The results for all six DSC curves are shown in **Table**. As can be seen, they almost coincide and differ by no more than 2%. According to [24, 25], in such cases, the error in determining thermal effects is no more than ±4%.

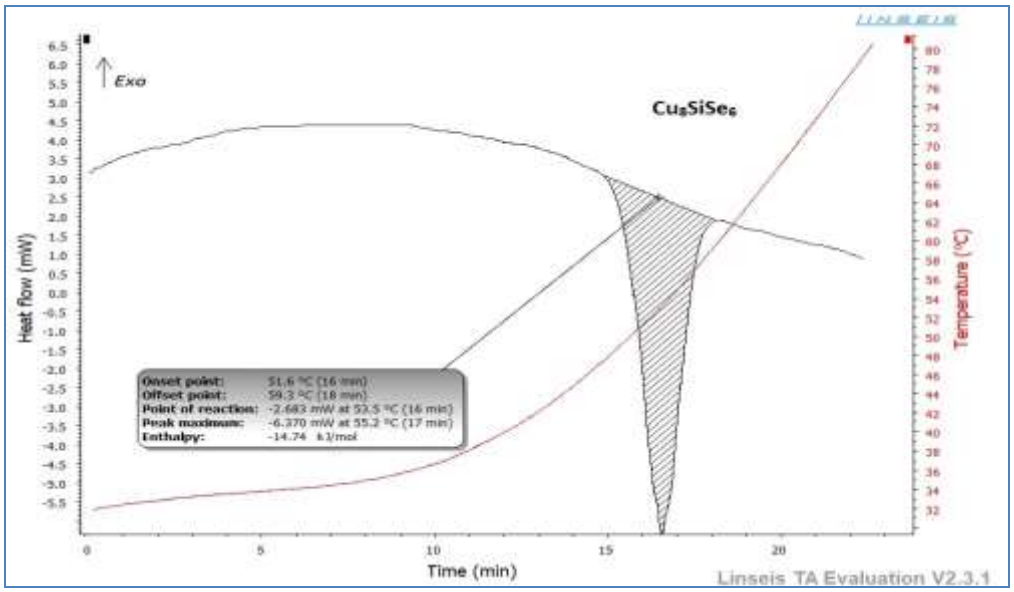

Fig. 2. Heating DSC curve for a Cu_8SiSe_6 compound sample with mass 28.75 mg

The final value of ΔHp.t for the Cu_8SiSe_6 compound was calculated as the average value of the experimentally obtained values (**Table**). The temperature of polymorphic transformation (325 K) of the Cu_8SiSe_6 was refined from the its DSC curves.

Since for first kind phase transitions $\Delta G_\alpha=\Delta G_\beta$, then $\Delta G=0$ in the Gibbs-Helmholtz equation:

$$\Delta G=\Delta H-T\cdot\Delta S$$

Then, for a phase transition of the first kind, we can write:

$$\Delta H_{p.t.}=T\cdot\Delta S_{p.t.}$$

From this relation, the entropy of the phase transition can be calculated:

$$\Delta S_{p.t.} = \Delta H_{p.t.}/T_{p.t.}$$

Using the last equation and the values of the enthalpy and the temperature (325 K) of the phase transition of the substance from the DSC data, we calculated the entropy of the phase transition of the studied compound (**Table**).

Table. Experimental DSC data and thermodynamic functions of the phase transition of the Cu_8SiSe_6 compound.

Sample weight, *mg*	**Experiment No**	**$T_{p.t.}$, *K***	**Experimental values of $-\Delta H_{p.t.}$, *kJ/mol***	**Average value of $-\Delta H_{p.t.}$, *kJ/mol***	**$\Delta S_{p.t.}$, *J/(mol·K)***
28.75	1	324.6	14.74	**14.73±0.59**	**45.32±1.81**
	2	325.0	14.87		
	3	325.1	14.59		
39.52	1	325.0	14.72		
	2	325.1	14.61		
	3	325.0	14.86		

Thus, the enthalpy and entropy of the phase transition of the Cu_8SiSe_6 compound at a temperature of 325 K were determined for the first time by the DSC method.

References

1. Babanly M.B., Yusibov Yu.A., Abishov V.T. Ternary chalcogenides based on copper and silver. Baku: BQU Publ.; 1993. 342 p. (In Russian)
2. Semkiv I., Ilchuk H., Pawlowski M., Kusnezh V. Ag_8SnSe_6 argyrodite synthesis and optical properties. *Opto-Electronics Review*. 2017, vol. 25, no. 1, pp. 37–40. https://doi.org/10.1016/j.opelre.2017.04.002
3. Studenyak I. P., Pogodin A. I., Studenyak V. I., Izai V. Y., Filep M. J., Kokhan O. P., Kúš P. Electrical properties of copper- and silver-containing superionic $(Cu_{1-x}Ag_x)_7SiS_5I$ mixed crystals with argyrodite structure. *Solid State Ionics.* 2020, vol. 345, pp. 115183-6. https://doi.org/10.1016/j.ssi.2019.115183
4. Lin S., Li W., Pei Y. Thermally insulative thermoelectric argyrodites. *Materials Today*. 2021, vol. 48, pp.198-213. https://doi.org/10.1016/j.mattod.2021.01.007
5. Fan, Y., Wang, G., Wang, R., Zhang, B., Shen, X., Jiang, P., … Zhou, X. Enhanced thermoelectric properties of p-type argyrodites Cu_8GeS_6 through Cu vacancy. *Journal of Alloys and Compounds.* 2020, vol. 822, pp. 153665-6. doi:10.1016/j.jallcom.2020.153665
6. Shen X., Yang C., Liu Y., Wang G., Tan H. A High Temperature Structural and Thermoelectric study of Argyrodite Ag_8GeSe_6. *ACS Appl. Mater. Interfaces.* 2019, vol. 11, no. 2. pp. 2168-2176. https://doi.org/10.1021/acsami.8b19819
7. Jin M., Lin S., Li W., Chen Z., Li R., Wang X. Pei Y. Fabrication and thermoelectric properties of single-crystal argyrodite Ag_8SnSe_6. *Chemistry of Materials.* 2019, vol. 31, no. 7, pp. 2603-2610. https://doi.org/10.1021/acs.chemmater.9b00393
8. Jiang B., Qiu P., Eikeland E., Chen H.,

Song Q., Ren D., Chen L. Cu_8GeSe_6-based thermoelectric materials with an argyrodite structure. *Journal of Materials Chemistry C*. 2017, vol. 5, no. 4, pp.943–952. https://doi.org/10.1039/C6TC05068A

9. Yang C., Luo, Y., Li X., Cui J. N-type thermoelectric Ag_8SnSe_6 with extremely low lattice thermal conductivity by replacing Ag with Cu. RSC Advances. 2021, vol. 11, no. 6, pp. 3732-3739. https://doi.org/10.1039/D0RA10454J
10. Ivanov-Shits A.K., Murin I.V. Solid state ionics, v.1. Saint Peterburg: SPU Publ.; 2000. 616 p. (In Russian).
11. Heep B. K., Weldert K. S., Krysiak Y., Day T. W., Zeier W. G., Kolb U., Snyder G. J., Tremel W. High Electron Mobility and Disorder Induced by Silver Ion Migration Lead to Good Thermoelectric Performance in the Argyrodite Ag_8SiSe_6. *Chem. Mater.* 2017, vol. 29, no. 11, pp. 4833−4839. https://doi.org/10.1021/acs.chemmater.7b00767
12. Lin Y., Fang S., Su D., Brinkman K.S. Enhancing grain boundary ionic conductivity in mixed ionic–electronic conductors. *Nat. Commun.* 2015, vol. 6, no. 1, pp. 1-9. https://doi.org/10.1038/ncomms7824
13. Gorochov O. Les composés Ag_8MX_6 (M = Si, Ge, Sn et X = S, Se, Te). *Bull. Soc. Chim. Fr.* 1968, pp. 2263–2275.
14. Moroz M.V., Prokhorenko M.V. Determination of thermodynamic properties of saturated solid solutions of the Ag–Ge–Se system using EMF technique. *Russian Journal of Electrochemistry*. 2015, vol. 51, no. 7, pp. 697-702. https://doi.org/10.1134/S1023193515070046
15. Moroz M.V., Prokhorenko M.V. Measurement of the thermodynamic properties of saturated solid solutions of compounds in the Ag-Sn-Se system by the EMF method. *Russian Journal of Physical Chemistry A.* 2015, vol. 89, no. 8, pp. 1325-1329. https://doi.org/10.7868/S0044453715080221
16. Alverdiyev J., Abbasova V.A., Yusibov Y.A., Babanly M.B. Thermodynamic properties of solid solutions in the Cu_8GeS_6 –Ag_8GeS_6 system. *Condensed Matter and Interphases*. 2017, vol. 19, no. 1, pp. 22–26.
17. Aliyeva Z.M., Bagheri S.M., Aliev Z.S., Alverdiyev I.J., Yusibov Yu.A., Babanly M.B. The phase equilibria in the Ag_2S–Ag_8GeS6–Ag_8SnS_6 system. *J. Alloys Compd.*, 2014, vol. 611, pp. 395–400.
18. Alverdiyev I.J., Aliev Z.S., Bagheri S.M., Mashadiyeva L F., Yusibov Y.A., Babanly M.B. Study of the $2Cu_2S$+ $GeSe_2$ ↔ $2Cu_2Se$+GeS_2 reciprocal system and thermodynamic properties of the $Cu_8GeS_{6x}Se_x$ solid solutions. *J. Alloys Compd.* 2017, vol. 691, pp. 255–262.
19. Moroz M.V., Prokhorenko M.V., Demchenko P.Yu., Reshetnyak O.V. Thermodynamic properties of saturated solid solutions of Ag_7SnSe_5Br and Ag_8SnSe_6 compounds in the Ag–Sn–Se–Br system measured by the EMF method. *J. Chem. Thermodyn*. 2017, vol. 106, pp. 228-231. https://doi.org/10.1016/j.jct.2016.12.004
20. Alverdiev I.D., Yusibov Y.A., Bagkheri S.M., Imamalieva S.Z., Babanly M.B. Thermodynamic study of Ag_8GeSe_6 by emf with an Ag_4RbI_5 solid electrolyte. *Russian Journal of Electrochemistry*. 2017, vol. 53, no. 5, pp. 551-554. https://doi.org/10.1134/S1023193517050032
21. Alverdiev I.D., Yusibov Y.A., Imamalieva S.Z., Babanly D.M., Tagiev D.B., Babanly M.B. Thermodynamic study of siver-tin selenides by the emf method with Ag_4RbI_5 solid electrolyte. *Russian Journal of Electrochemistry*. 2019, vol. 55, no. 5, pp. 467-474. https://doi.org/10.1134/S0424857019050025
22. Shpak O., Kogut Yu., Fedorchuk A., Piskach L., Parasyuk O. The Cu_2Se–$PbSe$–$SiSe_2$ System and the Crystal Structure of $CuPb_{1,5}SiSe_4$. *Науковий вісник Східноєвропейського національного університету імені Лесі Українки. Хімічні науки*. 2014, no. 21, pp. 39-47.
23. Ishii M., Onoda M., Shibata K. Structure and vibrational spectra of argyrodite family compounds Cu_8SiX_6 (X=S, Se) and Cu_8GeS_6. *Solid State Ionics.* 1999, vol. 121, no.(1-4), pp. 11–18. https://doi.org/10.1016/S0167-2738(98)00305-1

24. Hohne G.W.H., Hemminger W.F. Flammersheim H.J. Differential Scanning Calorimetry. Second Edition. Berlin: Springer. 2003
25. Menczel J., Grebowicz J. The Handbook of Differential Scanning Calorimetry: Techniques and Low Molecular Mass Materials. Elsevier Science. 2022. 858 p

Cu_8SiSe_6 BİRLƏŞMƏSİNİN FAZA KEÇİDİNİN TERMODİNAMIK FUNKSİYALARININ DSK ÜSULU İLƏ TƏYİNİ

Ü.R. Bayramova

AMEA Kataliz və Qeyri-üzvi Kimya İnstitutu
AZ 1143, H. Cavid pr. 113, e-mail ubayramova088@gmail.com

Xülasə: *Cu_8SiSe_6 üçlü birləşməsi diferensial skanedici kalorimetriya (DSK) üsulu ilə tədqiq edilmişdir. İki fərqli çəkidə olan nümünələrin DSK əyriləri əsasında bu birləşmənin aşağı temperaturlu ortorombik modifikasiyadan yüksək temperaturlu kubik quruluşa keçidinin temperaturu və entalpiyası ilk dəfə olaraq təyin edilmişdir. Gibbs-Helmholtz tənliyindən istifadə edilərək, tədqiq olunan birləşmənin faza keçidi entropiyası da hesablanmışdır.*
Açar sözlər: *Cu_8SiSe_6, diferensial skanedici kalorimetriya, faza keçidi, entalpiya, entropiya.*

ОПРЕДЕЛЕНИЕ ТЕРМОДИНАМИЧЕСКИХ ФУНКЦИЙ ФАЗОВОГО ПЕРЕХОДА СОЕДИНЕНИЯ Cu_8SiSe_6 МЕТОДОМ ДСК

У.Р. Байрамова

Институт Катализа и Неорганической химии Национальной АН Азербайджана
AZ 1143, пр. Г. Джавида, 113, e-mail: ubayramova088@gmail.com

Аннотация: *Методом дифференциально-сканирующей калориметрии (ДСК) исследовано тройное соединение Cu_8SiSe_6. На основании данных кривых ДСК двух образцов с различными массами определены температура и энтальпия фазового перехода от низкотемпературной орторомбической модификации к высокотемпературной кубической. Используя уравнение Гиббса-Гельмгольца была рассчитана также энтропия фазового перехода исследуемого соединения.*
Ключевые слова: *Cu_8SiSe_6, фазовый переход, энтальпия, энтропия, дифференциально-сканирующая калориметрия.*